Charge state of donor-acceptor quasi-one-dimensional systems

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The ground-state energy of quasi-one-dimensional donor-acceptor systems is calculated for an arbitrary amount of electrons transferred from the donors to electrons. It is found that electrostatic energy makes the main contribution to the energy in TTF–TCNQ crystals. A calculation of the energy shows that the number of excess electrons per acceptor molecule cannot be unity. The charge state of systems in which the electrostatic energy is comparable to the electron kinetic energy is also investigated.

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1. INTRODUCTION

Many recent papers[1-4] are devoted to the experimental investigation of the electrophysical properties of a new class of highly conducting organic molecular crystals. This class includes the charge transfer complexes TTF—TCNQ, the mixed-valence platinum complexes $K_2Pt(CN)_4Br_{0.3}\cdot 3H_2O$, and others. The most characteristic feature of these systems is the presence of peaks in the temperature dependence of the conductivity. Thus, for example, for certain TTF—TCNQ samples the conductivity at 60°K is higher by two orders of magnitude than at room temperature, and the largest value of the conductivity is $\sim 10^4-10^5\ (\Omega\text{-cm})^{-1}$, which is in general a record value for organic systems.

Another characteristic feature of high-conductivity system is the sharp anisotropy of their properties due to the peculiar packing of the molecules in these crystals. For example, the TTF—TCNQ crystals consist of alternating stacks of donor TTF molecules and TCNQ acceptors. The conductivity along the stacks is larger by two or three orders of magnitude than the conductivity in the direction perpendicular to the stacks, so that the crystals are in essence quasi-one-dimensional. At high temperatures (at $T > 60°$K in TTF—TCNQ) these systems are characterized by a negative temperature coefficient of electric conductivity and by the presence of a large parametric susceptibility, making these systems related to metals. When the temperature is lowered, these systems go over more or less abruptly to the semiconducting state. The physical nature of this transition is not yet clear. Its reason lies in the large number of possible instabilities that bring the one-dimensional system to a dielectric state. Let us list briefly the main types of instability.

a) Peierls instability, due to distortion of the lattice structure with appearance of a superstructure having a period $\hbar/2p_F$ (p_F is the electron quasimomentum on the Fermi surface).

b) Antiferromagnetic transition with formation of a gap in the one-electron spectrum, due to the electron repulsion. This transition competes as a rule with the Peierls transition.

c) Formation of a one-dimensional Wigner crystal in the one-dimensional chain (separately for the holes and electrons), owing to the long-range character of the Coulomb interaction.

d) Transition to the state of an exciton dielectric, in which the electrons and holes of two neighboring chains are bound together.

e) Finally, if the system is not subject to any of these transitions, it can become superconducting at low temperatures.

There exist well-defined and frequently exactly-solvable models for the description of all these transitions. The difficulty lies at present, however, in the correct determination of that model which describes the quasi-one-dimensional system. The complete Hamiltonian of such a system is quite easy to write out. It takes the form

$$\hat{H}=\hat{H}_x{}^A+\hat{H}_x{}^D+\alpha_A\hat{N}_A+\alpha_D\hat{N}_D+\hat{H}_M, \qquad (1.1)$$

where α_A and α_D are the one-electron energies of the acceptor (A) and donor (D) molecules, respectively, while $\hat{N}_A$ and $\hat{N}_D$ a re the electron-number operators for the molecules A and D. The Hubbard Hamiltonian $\hat{H}_X^A$ ($\hat{H}_X^D$) for the stacks A (D) is given by (for an individual stack)

$$\hat{H}_x=-\beta\sum_{n,\sigma}a^+_{n\sigma}(a_{n+1,\sigma}+a_{n-1,\sigma})+\gamma_0\sum_n a^+_{n\alpha}a_{n\alpha}a^+_{n\beta}a_{n\beta}, \qquad (1.2)$$

$a^+_{n\sigma}$ and $a_{n\sigma}$ are the operators for electron creation and annihilation of the n-th molecule, and $-\beta$ is the integral of electron transfer between neighboring molecules, with $\beta > 0$; γ_0 is the parameter of Coulomb repulsion of the electrons per molecule; $\hat{H}_M$ is the crystal electrostatic-energy operator.

The reduction of the system to one of the exactly-solvable model Hamiltonians depend on the ratio of the parameters of this total Hamiltonian. A particularly important role is played by the total number of holes and electrons in this system (their number divided by the total number of, say, the acceptor molecules will be designated ρ). Thus, for example, if $\rho = 1$ (in this case one speaks of complete transfer of the charge from the donors to the acceptors) the type of the transition is limited to cases (a) and (b). If $\rho < 1$ (as a rule the case $\rho > 1$ is not realistic), then (b) must be excluded from consideration. It should be stated that ρ depends on the energy parameters α, β, γ_0, etc. The purpose of this paper is to determine ρ for similar systems and, in particular, to prove that $\rho < 1$ for the concrete system TCNQ—TTF. We note in this connection that at present there are also experimental data that indicated incomplete charge transfer in TTF—TCNQ. Thus, it was concluded earlier[5] that $\rho \gtrsim 2/3$, on the basis of an analysis of the photoemission spectra of the neutral TTF and TCNQ molecules, of the $TCNQ^-$ ion, and also of TTF—TCNQ complexes.

2. VALUES OF THE DIFFERENT CONTRIBUTIONS TO THE SYSTEM HAMILTONIAN

Before we assess the relative roles of the various terms in (1.1), we make one remark. It turns out that $\gamma_0/\beta \gg 1$ for the TTF–TCNQ system (according to the estimates of[4] $\beta = 0.13$ eV, and the parameter previously obtained[6] by quantum-mechanical calculations of the TCNQ molecule is $\gamma_0 \approx 4$ eV). There are also grounds for expecting γ_0/β to be large also for other complexes. Therefore, in accord with the results of[7], it is legitimate to discard the second term in the Hamiltonian (12) and to consider spinless particles. The Hamiltonian (1.2) then reduces to the kinetic-energy operator $\hat{H}_{\text{kin}}$ of free spinless Fermi particles. The corresponding corrections to the energy are β^2/γ_0 and can be written out without difficulty. We note also that an analysis of the case when $\beta/\gamma_0 \approx 1$ raises no difficulties in principle and will be carried out, in particular, in Sec. 4.

We consider now the question of calculating the ground-state energy of (1.1). Since this is in general a very complicated problem, we shall attempt to represent the Hamiltonian (1.1) in the form $\hat{H} = \hat{H}_0 + \hat{H}_1$, such that $\hat{H}_0$ is sufficiently simple in form and $\hat{H}_1$ can be taken into account by perturbation theory. We choose $\hat{H}_0$ to be $\hat{H}_M + \alpha_A \hat{N}_A + \alpha_D \hat{N}_D$, and $\hat{H}_1$ to be $\hat{H}_{\text{kin}}$. It is easily seen that this subdivision is justified if $|\beta/M| \ll 1$, where M is the electrostatic energy per pair of molecules A and D (the Madelung energy), and the correction is $E_1 \sim \beta^2/M$. As will be shown later on, it is precisely this structure which is typical of TTF–TCNQ crystals. The Madelung energy is calculated for TTF–TCNQ in Sec. 3. It should be noted that in our case ρN electrons and ρN holes (N is the total number of acceptors) will be located on the molecules A and D in ordered fashion (one electron and one hole each on the molecule A or D).[1)] In other words, the ground state of the system will be ferroelectric and correspond to formation of a Wigner crystal. Another possible ground state of (1.1) is the metallic state. Then the electrons and holes are uniformly distributed over the molecules and $E_M = -M\rho^2/2$. This situation takes place at $M \lesssim \beta$. (The ground-state energy in the metallic phase is calculated in Sec. 4.)

We note also that in principle one cannot exclude a situation in which the energy of the ferroelectric and metallic states as functions of ρ have an intersection point. In this case the system will undergo a transition from the ferroelectric (dielectric of the Wigner-crystal type) to the metallic state.

3. ELECTROSTATIC ENERGY OF TTF–TCNQ CRYSTAL

We consider in this section the electron structure of the TTF–TCNQ crystal, neglecting the electron kinetic energy (i.e., in the electrostatic limit) at various degrees of charge transfer ρ. The problem then consists of determining the optimal value of ρ. In the employed approximation, electron hopping from one molecule to another is forbidden. Therefore at certain $\rho < 1$ the crystal, as already mentioned, consists of neutral and ionized pairs of TTF–TCNQ molecules. It is the ratio of the ionized TCNQ–TTF⁺ pairs to their total number which determines the value of ρ.

The need for such an investigation in order to determine the optimal ρ is seen from the following simple reasoning: Consider two infinite parallel strings made up of point charges q and –q (Fig. 1). The electrostatic energy of such a system per pair of molecules can obviously be written in the form

$$E_M = q^2 a^{-1}[-1 + 2g(a/l)], \tag{3.1}$$

where

$$g(x) = \sum_{n=1}^{\infty} [x/n - x(n^2+x^2)^{-1/2}]. \tag{3.2}$$

It follows from (3.1) and (3.2) that the sign of E_M can be arbitrary, depending on a/l. Thus, $E_M < 0$ if $l/a \gg 1$. Let us estimate the change ΔE of the total energy of the system when a pair of neighboring charges of opposite sign is annihilated. We have

$$\Delta E = q^2 a^{-1}(1 - 4g(a/l)). \tag{3.3}$$

If $1 < 4g(a/l)$ then $\Delta E < 0$. Thus, the total energy of the system in question can decrease when the number of charge pairs q and –q is decreased, even if $E_M < 0$. Consequently, at specified values of the lattice parameters (in this case a and l) it may turn out that the minimum of the total energy corresponds to $\rho < 1$.

Before we report the results of the calculation of the electrostatic energy of the TTF–TCNQ crystal, we present some information on the TTF and TCNQ molecules and on the geometry of the lattice of the crystal produced by them. The molecules TTF and TCNQ (Fig. 2) are typical representatives of conjugated systems characterized by the presence of electronic states that are delocalized over the entire molecule. Therefore on going from the neutral molecules to the corresponding ion-radicals TTF⁺ and TCNQ⁻, the excess charge becomes distributed over several atoms. The table lists the values of the charge on the atoms of these systems, as obtained from standard quantum-mechanical calculations.[8,9] Although the accuracy of the quantum-mechanical calculations of such molecules is limited (the charge distributions are subject to an error 5–20%), it suffices nevertheless, as will be demonstrated by the results, for the purposes of the present analysis. The

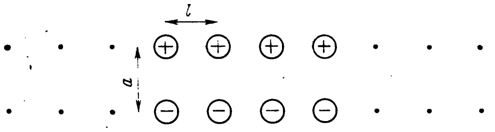

FIG. 1. Schematic representation of two strings with charges q –q.

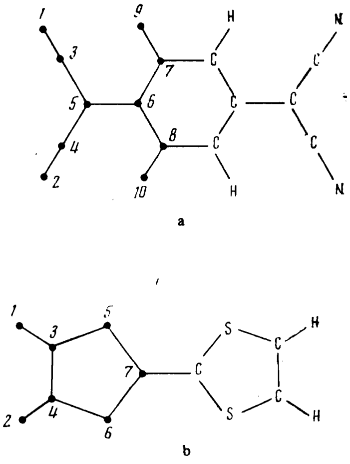

FIG. 2. Skeletons of the molecules TCNQ (a) and TTF (b).

Distribution of charges in the TCNQ and TTF molecules and ions

System	Number of atom					
	1	3	5	6	7	9
$TCNQ^-$	—0.3	0.15	—0.2	0	0	0
$TCNQ^0$	—0.19	0.14	0	0.1	0	0
TTF^+	0.1	0	0.15	0.15	0	—
TTF^0	0.04	0.01	—0.06	—0.06	0	—

geometry of the molecules TTF and TCNQ and of their ion radicals is known from data on the x-ray structure analysis of a number of molecular crystals.[10–12] The quantum-mechanical calculations[8] of the conformations of the free molecules TTF and TCNQ and ions $TCNQ^-$ and TTF^+ lead to practically the same values of the parameters of their geometric structure. Thus, the spatial structures of these compounds have been well investigated.

The lattice-parameters of the TTF—TCNQ crystal were published earlier.[12] The unit cell (Fig. 3) contains two molecules of each sort and constitutes a parallelepiped compressed along the b direction.

The system energy E is in general a function of the transferred charge ρ and of the geometric parameters of the lattice. Since, however, the system geometry is known,[12] it suffices to minimize E with respect to ρ in order to find the optimal value of ρ.

The electrostatic energy of the crystal was calculated by Ewald's method.[13] The systems $TCNQ^-$, TTF^+, TCNQ, and TTF were regarded in the calculation as aggregates of point charges. We proceed to discuss the results of the calculation of the Madelung energy of the TTF—TCNQ crystal at various values of the charge transfer parameters.

In the case $\rho = 1$, the crystal consists only of the ions $TCNQ^-$ and TTF^+. To estimate the influence of the character of the charge distribution over the $TCNQ^-$ and TTF^+ ions on the value of E_M, a detailed investigation was carried out in[14]. The results obtained by Ukrainskiĭ[14] can be formulated as follows: The Madelung energy depends little on the character of the charge distribution over the molecule, i.e., $E_M = (2 \pm 0.2)$ eV. Polarization of the ions lowers E_M by approximately 5—10%. The small effect of the polarization is due to the fact that the crystal has an inversion center. Thus, the inaccuracy in the calculation of the charge distribution in the ions is not significant.

In the case of incomplete charge transfer, i.e., at $\rho < 1$, as already noted, the crystal contains in the approximation in question both ions and neutral molecules. For each given ρ there exist then, generally speaking, several variants of the placement of the ions and molecules. The real situation will correspond, naturally, to the configuration with the minimal total energy. Some of the arrangements considered by us for the molecules and ions in the lattice are shown in Figs. 4 and 5 (for the values $\rho = 3/4, 2/3, 1/2, 1/3, 1/4$). These arrangements were chosen such that at a given ρ the distance between ions of the same sign is largest, and the distance between ions of opposite sign is the smallest. The Madelung energies per pair of ions, corresponding to the indicated values of ρ, are $E_M = -2.5, -2.7, -3.1, -3.2$, and -3.1 eV. We note that the role of the contribution of the polarization to E_M increases with decreasing ρ, since there are $(1 - \rho)/\rho$ pairs of neutral molecules for each pair of ions. Since allowance for the polarization always lowers E_M, the value of this energy at $\rho \lesssim 1/2$ can reach -4 eV. We note also that for $\rho = 1/3$ and $2/3$ the symmetry of the crystal field is violated—there is no inversion center. This results in additional polarization of the ions and molecules, which lowers EM somewhat more. According to our estimates, however, these corrections are small, since there is still no cancellation of the electric fields.

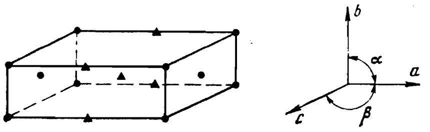

FIG. 3. Lattice of the TTF—TCNQ crystal. ▲, ●—centers of the molecules TCNQ and TTF, respectively, $\alpha = 90°$, $\beta = 104°46'$, a = 12.298 Å, b = 3.819 Å, c = 18.468 Å.

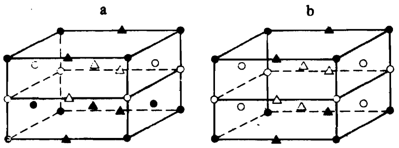

FIG. 4. Arrangements of the ions and molecules in the TFF—TCNQ crystal lattice at $\rho = 1/2$ (a) and $\rho = 3/4$ (b). △, ○—centers of the ions $TCNQ^-$ and TTF^+; ▲, ●—centers of the corresponding molecules. The lattice corresponding to $\rho = 1/4$ can be obtained from the lattice of Fig. 4b by the inversion ○, △ ⇌ ●, ▲.

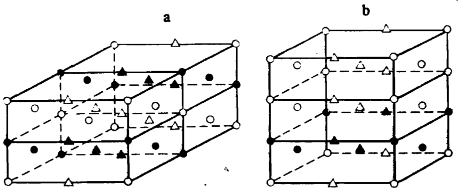

FIG. 5. Arrangement of the ions and molecules in the TTF—TCNQ crystal lattice for $\rho = 1/2$ (a) and $\rho = 2/3$ (b). The lattice corresponding to $\rho = 1/3$ can be obtained from that of Fig. 5b by the inversion ○, △ ⇌ ●, ▲.

Figure 6 shows a plot of the crystal energy per pair of TTF—TCNQ molecules$^{2)}$, $E(\rho) = \rho[E_M(\rho) + I - A]$, where I is the TTF ionization potential and A is the TCNQ electron affinity. (The difference I − A is equal to the energy gained on going from the pair of molecules TTF and TCNQ to the ions TTF^+ and $TCNQ^-$.)

An analysis of the experimental data on the TTF ionization potential[5] and on the electron affinity of TCNQ[15–17] shows that $(I - A) \approx 3$ eV. The solid curve in Fig. 3 was drawn through the points obtained by using the calculated values of $E_M(\rho)$ for $\rho = 1, 3/4, 2/3, 1/2, 1/3, 1/4$, and 0. The dashed curves take into account the possible calculation errors. As seen from the figure, the minimum of the energy lies in the region $1/4 < \rho < 2/3$.

4. CHARGE STATE IN THE METALLIC PHASE

We proceed now to calculate the ground-state energy of the system in the metallic phase. As already mentioned, the electrostatic energy of the system is given in this case by $-M\rho^2/2$, where M corresponds to the Madelung energy considered in the preceding section, at $\rho = 1$. Although a transition to spinless particles is possible at $\gamma_0/\beta \ll 1$, we consider here the total Hamilton-

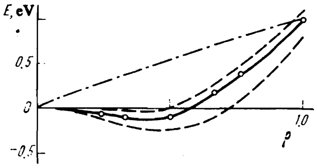

FIG. 6. Ground-state energy of the crystal TTF–TCNQ. Solid (and dashed) lines–energy of the ferroelectric phase, dash-dot line–energy of the metallic phase.

ian with spin taken into account, with an aim of investigating also the case $\gamma_0 = \beta$.

Thus, let us consider the system with Hamiltonian (1.1). We assume for simplicity that the integrals of electron transport in the donor and acceptor chains are equal ($\beta_A = \beta_D = \beta$), and that the integral of electron transport from a donor to an acceptor is small enough. We assume also that $\gamma_0^A = \gamma_0^D = \gamma_0$. Taking this into account, the Hamiltonian (1.1) becomes

$$\hat{H}=\alpha_A\hat{N}_A+\alpha_D\hat{N}_D-\beta\sum_{i\sigma}a_{i\sigma}^+(a_{i+1,\sigma}+a_{i-1,\sigma})-\beta\sum_{j\sigma}c_{j\sigma}^+(c_{j+1,\sigma}+c_{j-1,\sigma})$$
$$+\gamma_0\sum_i a_{i\alpha}^+a_{i\alpha}a_{i\beta}^+a_{i\beta}+\gamma_0\sum_j c_{j\alpha}^+c_{j\alpha}c_{j\beta}^+c_{j\beta}-NM\rho^2/2,\quad M>0, \tag{4.1}$$

where the operators $a_{i\sigma}$ and $c_{j\sigma}$ pertain respectively to the stacks A and D. The problem of finding the ground-state energy of a system with the Hamiltonian (4.1) can be solved exactly. It will be shown that for donor-acceptor systems described then by the Hamiltonian (4.1) the charge transfer ρ can assume any value from zero to unity and depends on the parameters contained in (4.1).

The ground state energy of (4.1) at $0 < \rho < 1$ is given, apart from an inessential constant, by

$$E/N=2E_x(\rho)+(\alpha_A-\alpha_D-\gamma_0)\rho-M\rho^2/2, \tag{4.2}$$

where $E_x(\rho)$ is the energy of the ground state of the Hubbard Hamiltonian, and $\alpha_A - \alpha_D - \gamma_0) = (I - A)$. The expression for $E_x(\rho)$ is[18]

$$E_x(\rho)=-2\beta\int_{-Q}^{\bar{Q}}dk\cos k\varphi(k), \tag{4.3}$$

and φ(k) and Q satisfy the equations

$$\int_{-Q}^{Q}dk\,\varphi(k)=\rho,\quad 2\pi\varphi(k)=1+8\pi u^{-1}\cos k\int_{-Q}^{Q}dk'\varphi(k')R[4u^{-1}(\sin k-\sin k')], \tag{4.4}$$

where

$$R(x)=(4\pi)^{-1}\int_{-\infty}^{\infty}\frac{dt\,\mathrm{sech}(\pi t/2)}{1+(x+t)^2},\qquad u=\gamma_0/\beta.$$

At $u \gg 1$ the expression for the energy $E_x(\rho)$ can be expanded in powers of u^{-1} and accurate to terms u^{-2} we have[7]

$$\frac{E_x(\rho)}{\beta}=-2\pi^{-1}\sin\pi\rho-4\ln 2u^{-1}\rho^2\left(1-\frac{\sin 2\pi\rho}{2\pi\rho}\right). \tag{4.5}$$

To find the charge transfer ρ we minimize (4.2) with respect to ρ. At $u \gg 1$ the quantity $E_x(\rho)$ in (4.2) is of the form (4.5), while the values of $E_x(\rho)$ and of $\partial E_x(\rho)/\partial\rho$ at $u \approx 1$ were obtained by numerical solution of Eqs. (4.4) and analogous equations for $\partial Q/\partial\rho$ and $\partial\varphi(k)\partial\varphi$ by reducing the corresponding integral equations to a system of 41 algebraic equations.

We consider first the case M = 0. The ρ(I – A) plot is given in Fig. 7 (solid curve). The range of values of I – A for which $0 < \rho < 1$ is bounded by the points x_1 and x_2. At arbitrary u we have $x_2 = 4\beta$ and $x_1 = (\Delta E_0 - \gamma_0)$, where ΔE_0 is the gap in the Hubbard model at $\rho = 1$. (At $u \gg 1$ we have $x_1 = -4\beta + 8\ln 2\beta u^{-1}$).

An analysis of expression (4.2) with $M \neq 0$ shows that there exists a critical value M_c of the Madelung constant, and at $M > M_c$ the charge transfer is either nonexistent ($\rho = 0$) or corresponds to transfer of one electron ($\rho = 1$). A plot of ρ(I – A) at $M > M_c$ is shown in Fig. 7 (dashed line). At $M < M_c$ there exists a region of values of (I – A) where $0 < \rho < 1$ (i.e., there is a partial charge transfer). It is also of interest to note that at the boundaries of this region the continuity of ρ(I – A) is violated and jumps appear to the values $\rho = 0$ and $\rho = 1$. Let us consider the case $u \gg 1$. Then $M_c = 4\pi\beta$. The jump (at $M \ll M_c$) at the extreme points of the region is given by $|\Delta\rho| = M/4\pi^2\beta$.

The dependence of ρ on (I – A) at $u \gg 1$ is shown in Fig. 8, and at u = 1 in Fig. 9 (M_c is equal to 6.4β at u = 1).

5. DISCUSSION OF RESULTS

The results obtained in Secs. 3 and 4 offer evidence that the charge transfer in TTF–TCNQ crystals is incomplete. Although a number of approximations, discussed in detail in Sec. 3, were used in the calculation of the ground-state energy, and consequently the exact value of the transferred charge cannot be indicated, it can be stated that it ranges from ¼ to ⅔. As seen from Fig. 6, the energy of the ferroelectric ground state is lower than the energy of the metallic phase at all ρ. This is perfectly natural, since the parameter β/M in TTF-TCNQ is much less than unity, so that the corrections needed to account for the kinetic energy are small. Examination of the transfer in other crystals containing D and A molecules calls for concrete calculations of the Madelung energy and for comparison of the ground-state energies in the ferroelectric and metallic phases. The energy of the latter in the general case was calculated in Sec. 4. As shown in Sec. 4, even in the case of low values of the Madelung constant ($M \lesssim \beta$), when the metallic phase is realized, the charge transfer will not be complete at certain definite values of the system parameters.

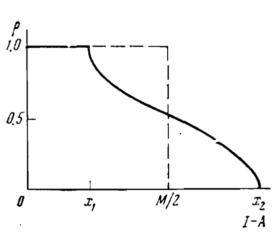

FIG. 7

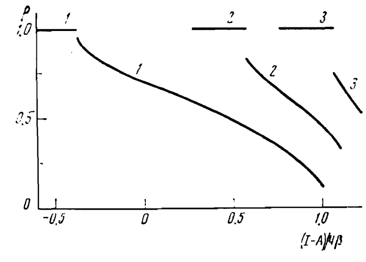

FIG. 8

FIG. 7. Plot of ρ against I – A at M = 0 (solid line) and at $M > M_c$ (dashed).

FIG. 8. Plots of ρ against I – A ($M < M_c$, u = 10): 1) $M = 0.16 M_c$, 2) $M = 0.48 M_c$, 3) $M = 0.64 M_c$.

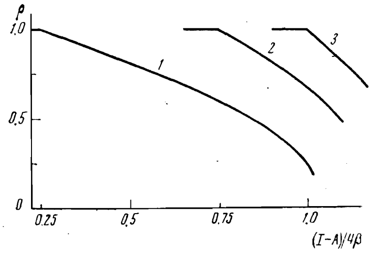

FIG. 9. Plots of ρ against I – A ($M < M_c$, u = 1): 1) $M = 0.31 M_c$, 2) $M = 0.62 M_c$, 3) $M = 0.77 M_c$.

Let us dwell in conclusion on the nature of the ground state of TTF—TCNQ crystals. Although according to all the foregoing this system is a Wigner-crystal ferroelectric and it might seem that the gap for the current excitation differs from zero, a more accurate analysis is required to ascertain whether this system is a dielectric or a metal. To explain the foregoing, consider a one-dimensional string with a Hamiltonian in the form

$$\hat{H}_1=-\beta\sum_{n=1}^{N}a_n^+(a_{n+1}+a_{n-1})+\gamma_{12}\sum_{n}a_n^+a_na_{n+1}^+a_{n+1}, \qquad (5.1)$$

where γ_{12} is the Coulomb interaction constant of electrons located on neighboring centers. As shown in[7], such a Hamiltonian describes a Fermi gas at $\gamma_0/\beta \gg 1$, neglecting the interaction of the electrons on non-neighboring centers. It is known[19] that at $\rho = 1/2$ (ρ is the number of electrons per center) and $\gamma_{12} > 2\beta$ the system described by the Hamiltonian (5.1) is a dielectric. We now assume that $\rho = 1/2 + \epsilon(\gamma_{12} > 2\beta)$ and let $\epsilon < 1$. This situation is precisely typical of TTF—TCNQ complexes. Then ϵN electrons will fill the upper (empty) band and the system becomes a metal.

The foregoing reasoning is qualitative in character. To ascertain whether the system remains a metal it is necessary to take into account the Coulomb interaction of electrons located not only on neighboring centers. At the same time, it demonstrates the principal difficulty when it comes to determining whether a TCNQ—TTF system will be a metal or a dielectric.

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[1] We make the following remark in this connection. In the TTF—TCNQ system there is an hierarchy of energies. The highest energies determine the distribution of the electrons in the individual molecules. According to quantum-mechanical calculations, the electronic state of the TTF^+ or $TCNQ^-$ ions is close to their state in vacuum. Therefore there can be no electrons or holes in the spaces between the molecules and the charge state, i.e., the number of ions in the system, is determined by the electrostatic energy E_M. On the other hand, the delocalization of the electrons and holes depends on the parameter $\beta/E_M \ll 1$. In this situation, only the entire number of electrons can be transferred, since the Hamiltonian of the electrostatic energy contains only the operators of the numbers of the particles on the centers, which have values zero and unity.

[2] The function $E(\rho)$ is not a function in the usual sense, since it has a break at each rational value of ρ.

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